THE PRACTICAL USE OF RESISTANCE MODELING TO INTERPRET THE GAS SEPARATION PROPERTIES OF HOLLOW FIBER MEMBRANES

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Abstract. A simple resistance modeling methodology is presented for gas transport through asymmetric polymeric membranes. The methodology allows fine structural properties such as active layer thickness and surface porosity, to be determined from experimental gas permeation data. This paper, which could be regarded as a practical guide, shows that resistance modeling, if accompanied by realistic working assumptions, need not be difficult and can provide a valuable insight into the relationships between the membrane fabrication conditions and performance of gas separation membranes.

Key Words: Hollow fiber membranes, gas separation properties, resistance modeling, fine structural details

1.0 INTRODUCTION
Knowledge of fine structural details at the microscopic level is important in a membrane development as it allows more complete understanding of the relationships between fabrication conditions and membrane performance. Such knowledge could be acquired through resistance modeling [1-6].

Resistance modeling involves the construction of an electrical resistance analogue to represent gas permeation. Each resistance is expressed in term of an appropriate flow equation. A parameter fit exercise using experimental data can then yield structural details such as active layer thickness and surface porosity.

A major breakthrough in the fabrication of gas separation membranes occurred in the early 1980's. Hines and Tripodi [7,8] pioneered the production of polysulfone hollow fiber membranes with acceptable flux and selectivity. They employed a silicone coating technique to repair defects in the membrane wall and introduced resistance modeling to rationalize the coating process.

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Fouda et al. [9] introduced a more realistic resistance approach called the *Wheatstone bridge model* in order to fit actual gas permeation results to possible membrane structures. A modified version of the *Wheatstone bridge model* was used by Shilton et al. [10]. They explicitly incorporated an expression for *Knudsen diffusion* and were able to predict the pore size as well as other structural parameters from experimental permeation data. The model also showed the ability to estimate the intrinsic selectivity of the solid polymer within the membrane and correlated it with the rheological conditions during fabrication.

The solution of a resistance model is essentially based on an n-dimensional parameter fit exercise and, as such, convergence difficulties can be encountered. In fact, the more sophisticated the model, i.e. the greater the number of parameters, the more capricious its behaviour can be. However, accompanied by pragmatic working assumptions, resistance modeling need not be difficult. The current paper presents the use of a practical resistance model where the fine structural properties of hollow fiber membranes are easily determined from gas permeation properties. This structural information can then be used to interpret the relationships between spinning conditions and membrane performance.

### 2.0 THEORY AND DEVELOPMENT OF RESISTANCE MODEL

#### 2.1 Membrane Structure and Resistance Analogues

Schematic structures of uncoated and coated asymmetric membranes, and the corresponding electrical circuit analogues, are shown in Figures 1 and 2.

![Figure 1](image)

**Figure 1** Schematic Diagram of a Uncoated Asymmetric Membrane and the Corresponding Electrical Circuit Analogue
which called the process of going from a possible resistance model was used to resist structural and electrical properties can be shown to be within the scope of fabrication. Two-dimensional models for these circular structures are easily made. The formation can be realized only in certain conditions and dimensions, and the corresponding followers of the previous section 1 and 2, respectively. Five gas transport regions are identified and hence the existing resistance can be represented by the membrane skin layer (R_1), the pores or imperfections in the skin (R_2), the silicone coating layer (R_3), the silicone pore penetration depth plus overlay height (R_4), and the macroporous substructure (R_5).

### 2.2 Resistance Model Equations

The overall resistances to gas transport in uncoated (RU) and coated (RC) membranes can be expressed as follow (R_3 is deemed negligible):

\[
\frac{1}{RU} = \frac{1}{R_1} + \frac{1}{R_2} \tag{1}
\]

\[
\frac{1}{RC} = \frac{1}{R_1 + R_3 + R_2 + R_4} \tag{2}
\]

The permeation of a gas through a membrane can be described by the pressure-normalized flux, \( P \), according to Equation (3):

\[
P = Q/(LMΔp) \tag{3}
\]

and the resistance to permeation (R) can be defined as:

\[
R = 1/(PA) \tag{4}
\]
Using Equations (1) - (4) and flow equations for solution diffusion as well as Knudsen diffusion, which have been described elsewhere [10], the following resistance model equations can be stated:

\[ P_{\text{Uncoated}} = \frac{P_{\text{polymer}}}{L_1} + \frac{1}{3} \frac{1}{\sqrt{2 \pi R_g T M_i}} \frac{r}{L_1} A_p, \]  
(5)

\[ P_{\text{Coated}} = \frac{P_{\text{polymer}}}{L_1} + \frac{1}{3} \frac{L_4}{\sqrt{2 \pi R_g T M_i}} \frac{L_1}{r A_j}. \]  
(6)

The selectivity \( \alpha \) of a membrane towards two gases \( i \) and \( j \) is simply defined as the ratio of the pressure-normalized fluxes:

\[ \alpha_j' = \frac{P_i}{P_j}. \]  
(7)

2.3 Working Assumptions and Use of Model Equations

When using the resistance model with experimental data, a number of simplifications become necessary and are implicit in the Equations (1) - (6).

The simplifications are as follow:

1. \( A_p \ll 1 \), hence the area of the solid polymer equals the membrane area \( A \).
2. \( L_4 \ll L_5 \), hence, on coating, the length of open pore for Knudsen diffusion equals \( L_1 \).
3. On coating, the resistance offered by the outer silicone layer \( R_5 \) is negligible.

Also, in gas separation membranes, surface defects or pores tend to be imperceptible. Electron micrographs do not reveal pores in the fiber walls even at magnification as high as \( \times 10,000 \), which suggests that pore radius \( r \) is not bigger than 100 Å [10]. Therefore, in resistance modeling of gas separation membranes, it is reasonable to assume that \( r = 100 \) Å (Knudsen flow range).

This assumption was employed in this work.

Equations (5) and (6) can be solved using experimentally determined pressure-normalized fluxes for two gaseous penetrants.

As reported previously [11], polysulphone hollow fiber membranes were fabricated using a dry/wet spinning process at two dope extrusion rates [11]. The gas permeation data of these membranes are shown in Tables 1 and 2, respectively and are used as specimen input data. However, the resistance modeling procedure can be used as a general utility that can be applied to any permeation data.
as well as the following

\begin{equation}
(5)
\end{equation}

\begin{equation}
(6)
\end{equation}

As early mentioned, the resistance modeling is basically a \( r \)-dimensional parameter fit exercise and, as such, is sensitive to the input data. Convergence problems and/or instability may occur with a particular range of input values. These problems were in fact encountered upon the data applying presented in Tables 1 and 2. To overcome such problems, further pragmatic assumptions have to be made.

In Table 1, flow through pores is significant as selectivities are fairly low. Structural properties (\( J_s \) and \( A_s \)) were therefore deduced exclusively from uncoated data, using Equation (5) for the two gaseous penetrants.

In the case of Table 2, the selectivities are high for the coated membranes and many values surpass the recognized polysulfone intrinsic selectivity of 28 for \( \text{CO}_2 \)/\( \text{CH}_4 \) [12]. Consequently, the flow through pores was regarded to be insignificant in these membranes. The \( L_s \) values were therefore calculated using the following abridged version of Equation (6), using the \( \text{CO}_2 \) data:

\begin{equation}
P_{i, \text{coated}} = \frac{P_{\text{polymer}, i}}{L_i}
\end{equation}

\( A_s \) was in turn calculated from the uncoated pressure-normalized flux for \( \text{CO}_2 \) using Equation (5).

The intrinsic gas permeation properties of the polymer (polysulfone) and coating material (polymethylsiloxane) for the penetrant gases (\( \text{CO}_2 \) and \( \text{CH}_4 \)) are given in Table 3.

Table 1 Gas Permeation Properties of Polysulfone Hollow Fiber Membranes Span x Relative Low Dope Extrusion Rate

<table>
<thead>
<tr>
<th>Module</th>
<th>( P_{\text{CO}_2} )</th>
<th>Uncoated ( \alpha_{\text{CO}_2}^{\text{CO}_2} )</th>
<th>Coated ( \alpha_{\text{CO}_2}^{\text{CO}_2} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>LO1</td>
<td>69.4</td>
<td>1.30</td>
<td>35.4</td>
</tr>
<tr>
<td>LO2</td>
<td>67.0</td>
<td>1.35</td>
<td>39.5</td>
</tr>
<tr>
<td>LO3</td>
<td>45.1</td>
<td>1.83</td>
<td>33.5</td>
</tr>
<tr>
<td>LO4</td>
<td>45.8</td>
<td>2.93</td>
<td>24.2</td>
</tr>
<tr>
<td>LO5</td>
<td>49.4</td>
<td>1.30</td>
<td>32.1</td>
</tr>
<tr>
<td>LO6</td>
<td>43.7</td>
<td>1.22</td>
<td>23.7</td>
</tr>
<tr>
<td>LO7</td>
<td>37.8</td>
<td>2.05</td>
<td>26.3</td>
</tr>
<tr>
<td>LO8</td>
<td>65.2</td>
<td>1.39</td>
<td>68.7</td>
</tr>
</tbody>
</table>

The spinning dope, which contained 22\% (w/w) polysulfone was extruded at a rate of 1.0 cm\(^3\)/min.

The stretch ratio was maintained at 1.

Pressure-normalized flux \( \times 10^6 \) (cm\(^3\))/(STP)/s cm\(^2\) cmHg measured at 25°C and at a pressure difference of 5 bar.
Further calculations of pore number, \( N_p \) and distance between pores, \( d_p \) were found easy to be obtained using Equations (9) and (10):

\[
N_p = A_p / (\pi d_p^2),
\]

\[
d_p = N_p^{-1/2}
\]

Table 2: Gas Permeation Properties of Polysulfone Hollow Fiber Membranes Spun at Relatively High Dope Extrusion Rate* [11]

<table>
<thead>
<tr>
<th>Module</th>
<th>Uncoated</th>
<th>Coated</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( P_{CO_2} )</td>
<td>( P_{CO_2} )</td>
</tr>
<tr>
<td>H1</td>
<td>64.20</td>
<td>1.71</td>
</tr>
<tr>
<td>H2</td>
<td>80.70</td>
<td>1.63</td>
</tr>
<tr>
<td>H3</td>
<td>98.20</td>
<td>2.18</td>
</tr>
<tr>
<td>H4</td>
<td>76.50</td>
<td>2.65</td>
</tr>
<tr>
<td>H5</td>
<td>81.30</td>
<td>2.64</td>
</tr>
<tr>
<td>H6</td>
<td>79.80</td>
<td>2.31</td>
</tr>
<tr>
<td>H7</td>
<td>54.80</td>
<td>3.69</td>
</tr>
<tr>
<td>H8</td>
<td>57.50</td>
<td>4.15</td>
</tr>
<tr>
<td>H9</td>
<td>62.50</td>
<td>3.30</td>
</tr>
</tbody>
</table>

* The spinning dope, which contained 22% (w/w) polysulfone was extruded at a rate of 2.5 cm/min. The stretch ratio was maintained at 1.5. Pressure-normalized flux \( \times 10^6 \) (cm³(STP)/h cm² cmHg) measured at 25°C and at a pressure difference of 5 bar.

Table 3: Intrinsic Gas Permeation Properties of Polysulfone and Polydimethylsiloxane

<table>
<thead>
<tr>
<th>Polymer</th>
<th>( P_{CO_2}^* )</th>
<th>( P_{CH_4} )</th>
<th>( P_{CO_2} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polysulfone</td>
<td>4.5³</td>
<td>0.16</td>
<td>28³</td>
</tr>
<tr>
<td>Polydimethylsiloxane</td>
<td>3250³</td>
<td>950³</td>
<td>3.4</td>
</tr>
</tbody>
</table>

* Permeability coefficient \( \times 10^{10} \) (cm³(STP)/h cm² cmHg).

3.0 RESULTS AND DISCUSSION

The membrane fire structural properties determined using the resistance modeling procedure, shown in Tables 4 and 5, respectively, are for the two sets of hollow fiber membranes. When the details are viewed in correlation the permeation data presented in Tables 1 and 2, a number of observations could be made.
Table 4 Fine Structural Properties Determined by Resistance Modeling - Polysulfone Hollow Fiber Membranes Spun at Relatively Low Dope Extrusion Rate

<table>
<thead>
<tr>
<th>Module</th>
<th>Thickness of active layer, ( L_1 ) (Å)</th>
<th>Surface porosity, ( A_p ) (cm(^2)/cm(^3)) ( \times 10^{-4} )</th>
<th>Pore number, ( N_p ) (cm(^{-3})) ( \times 10^3 )</th>
<th>Distance between pores, ( d_p ) (Å) ( \times 10^6 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>LO1</td>
<td>1116</td>
<td>1.136</td>
<td>3.618</td>
<td>1.663</td>
</tr>
<tr>
<td>LO2</td>
<td>1191</td>
<td>1.060</td>
<td>3.374</td>
<td>1.721</td>
</tr>
<tr>
<td>LO3</td>
<td>1657</td>
<td>0.630</td>
<td>2.006</td>
<td>2.233</td>
</tr>
<tr>
<td>LO4</td>
<td>1210</td>
<td>0.318</td>
<td>1.011</td>
<td>3.544</td>
</tr>
<tr>
<td>LO5</td>
<td>1661</td>
<td>1.130</td>
<td>3.598</td>
<td>1.667</td>
</tr>
<tr>
<td>LO6</td>
<td>1994</td>
<td>1.282</td>
<td>4.080</td>
<td>1.566</td>
</tr>
<tr>
<td>LO7</td>
<td>1949</td>
<td>0.528</td>
<td>1.681</td>
<td>2.439</td>
</tr>
<tr>
<td>LO8</td>
<td>1193</td>
<td>1.000</td>
<td>3.183</td>
<td>1.772</td>
</tr>
<tr>
<td>Average</td>
<td></td>
<td>0.885</td>
<td>2.819</td>
<td>2.026</td>
</tr>
</tbody>
</table>

Table 5 Fine Structural Properties Determined by Resistance Modeling - Polysulfone Hollow Fiber Membranes Spun at Relatively High Dope Extrusion Rate

<table>
<thead>
<tr>
<th>Module</th>
<th>Thickness of active layer, ( L_1 ) (Å)</th>
<th>Surface porosity, ( A_p ) (cm(^2)/cm(^3)) ( \times 10^{-4} )</th>
<th>Pore number, ( N_p ) (cm(^{-3})) ( \times 10^3 )</th>
<th>Distance between pores, ( d_p ) (Å) ( \times 10^6 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>HI1</td>
<td>948</td>
<td>0.485</td>
<td>1.537</td>
<td>2.551</td>
</tr>
<tr>
<td>HI2</td>
<td>1181</td>
<td>1.535</td>
<td>4.885</td>
<td>1.431</td>
</tr>
<tr>
<td>HI3</td>
<td>822</td>
<td>0.820</td>
<td>2.609</td>
<td>1.958</td>
</tr>
<tr>
<td>HI4</td>
<td>890</td>
<td>0.652</td>
<td>2.076</td>
<td>2.195</td>
</tr>
<tr>
<td>HI5</td>
<td>896</td>
<td>0.848</td>
<td>2.700</td>
<td>1.524</td>
</tr>
<tr>
<td>HI6</td>
<td>1046</td>
<td>1.172</td>
<td>3.730</td>
<td>1.657</td>
</tr>
<tr>
<td>HI7</td>
<td>922</td>
<td>0.169</td>
<td>0.538</td>
<td>4.311</td>
</tr>
<tr>
<td>HI8</td>
<td>877</td>
<td>0.166</td>
<td>0.528</td>
<td>4.352</td>
</tr>
<tr>
<td>HI9</td>
<td>775</td>
<td>0.105</td>
<td>0.334</td>
<td>5.473</td>
</tr>
<tr>
<td>Average</td>
<td></td>
<td>0.661</td>
<td>2.106</td>
<td>2.870</td>
</tr>
</tbody>
</table>

The pressure-normalized flux was found to increase with the increase in the dope extrusion rate. This can be explained by a decrease in active layer thickness as determined by the modeling. Taking a straightforward view, if membranes are defect free, the active layer thickness has little influence on selectivity [14,15]. However, if defects arise, the thinner the active layer, the more selective is the membrane. The high selectivities of the high dope extrusion rate hollow fibers can be rationalized by the resistance modeling:
these membranes have relatively thin skins and lower surface porosities. Thus, the increase in the dope extrusion rate results in a membrane structure that cause an increase in both pressure-normalized flux and selectivity, two key properties commonly thought to compete rather than increase simultaneously.

It is likely believed that the thinner active layer and lower surface porosity of the high extrusion rate membranes are related to the lower dry gap residence time in the spinning process. The dry gap is considered to be responsible for skin formation [16] and hence the residence time is found to be a critical factor.

Also, many of the higher dope extrusion rate fibers exhibit selectivities beyond the recognized polysulfone intrinsic value of 28 for CO$_2$/CH$_4$[12]. This implies that rheological effects are inclusive. The higher levels of shear experienced in the spinneret may orient the polysulfone molecules, causing an enhancement in selectivity. FTIR spectroscopic studies have supported this view [11].

The values of $d_p$ allow visualization of the pore landscape. The values show that if the pores were magnified to 1 cm diameter, the adjacent pores would be about 10 meters away in the low dope extrusion rate membranes and about 15 meters away in the high dope extrusion rate membranes. In view of the uncoated selectivities, this illustrates how damaging a limited number of pinholes can be in gas separation membranes.

4.0 CONCLUSION
In conclusion, this paper has illustrated that resistance modeling can be used in a simple way to deduce fine structural properties of gas separation membranes. The structural information can then be used to help interpret the relationships between fabrication conditions and performance.

REFERENCES


SYMBOLS

\( A \) Membrane surface area \((\text{cm}^2)\)

\( A_p \) Fraction of membrane surface area that is pores (surface porosity) \((\text{cm}^2/\text{cm}^2)\)

\( d_p \) Distance between pores \((\text{Å})\)

\( L \) Thickness \((\text{Å})\)

\( M \) Molecular Weight \((\text{g/mol})\)

\( N_p \) Number of pores per unit membrane surface area \((\text{cm}^{-2})\)

\( \Delta p \) Pressure difference \((\text{cmHg})\)

\( P \) Permeability Coefficient \((\text{cm}^3\text{(STP)/cm/s cm}^2\text{ cmHg})\)

\( P \) Pressure-normalized flux \((\text{cm}^3\text{(STP)/s cm}^2\text{ cmHg})\)

\( Q \) Flowrate \((\text{cm}^3\text{(STP)/s or moles/s})\)

\( R_0 \) Universal Gas Constant \((\text{J/mole K})\)

\( R \) Resistance to Gas Permeation \(((\text{s cmHg)/cm}^3\text{(STP)})\)

\( R \) Radius of pore \((\text{Å})\)

\( T \) Temperature \((\text{K})\)

\( \alpha \) Selectivity \((-)\)

CLASSIFICATION/SUBSCRIPTS

1 Membrane active layer
2 Pore
3 Silicone coating layer
4 Silicone pore overlay plus penetration
5 Macroporous substructure
6 Uncoated
7 Coated
8 Component \(i\) \((\text{CO}_2)\)
9 Component \(j\) \((\text{CH}_4)\)